

## Amendments to the Specification

Please replace the Abstract with the attached amended/substitute Abstract. A marked-up version of the Abstract follows:

### **ABSTRACT**

~~The present invention describes a generic methodology to formulate a composite solid~~  
~~useful for catalyzing variety of reactions, the present invention in particular relates to a A~~  
heterogeneous catalyst includes ~~as a formulation constituting~~ a solid support having deposited  
thereon a catalytically active material, which is substantially ~~practically~~ insoluble in organic  
and aqueous ~~variety of liquid media;~~ ~~The~~ ~~the~~ said insoluble material is constructed from  
secondary building blocks derived from suitable organometallic active components, and the  
organometallic active component may be ~~is~~ molecularly modified so as to introduce two or  
more anionic ~~negatively charged~~ functional groups. ~~These, these~~ molecularly modified  
organometallic components, upon interaction with salts of  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ , provide the  
practically insoluble solid material. Methods ~~and the invention further ascertains various~~  
~~ways of formulating the organometallic active materials material~~ on a solid support as a solid  
catalyst are also provided. ~~The catalysts are capable of, the methodology is suitable for~~  
~~preparation of wide variety of catalysts having applications in catalyzing diverse reactions in~~  
polar and nonpolar reaction media, and the overall integrity of the formulation as a solid  
material in a liquid phase provides easy catalyst and product separation.

Please replace the paragraph beginning on page 2, line 20, with the following  
rewritten paragraph:

It is however recognized that catalytic activity is low in biphasic medium due to  
limited solubility of organic reactants in the catalyst phase. Moreover such biphasic reactions  
require high reactor pressure in case of gas-liquid reactions. To achieve practical rates of

reactions catalyst loading has to be increased or alternatively using larger process equipment, which is usually cost prohibitive. Further, these reactions require numerous accessory devices ~~equipment's~~ to separate liquid-liquid fractions under reaction conditions.

Please replace the paragraph beginning on page 4, line 26, with the following rewritten paragraph:

It has now been discovered that reactions that are catalyzed otherwise by a soluble catalyst can now be catalyzed by the solid catalyst of this invention. The solid catalyst as described ~~said~~ herein is not a chemically defined single component catalyst system, but a formulation wherein a solid support and a catalytically active material are assembled together to form a solid catalyst. The support is components, which by itself is ~~a~~ catalytically inactive but provides a physical vehicle, filler, and provides ~~provide~~ a high surface area whereupon catalytically active material is placed. This conglomerate of support and catalytically active material is not a simple random physical mixture, but is assembled in a specific manner such that support surface is covered or deposited with catalytically active material. Such concepts are known earlier as described in the background of the invention but providing a catalyst suitable only for gas phase or for specific liquid phases, for ~~For~~ example, supported aqueous phase catalysts (hereafter termed as SAPC) or supported liquid phase catalysts (hereafter termed as SLPC). SAPC for instance can only be employed in cases where reaction medium is water immiscible organic media. Similarly, SLPC are suitable only in gas phase but not in general liquid phases.

Please replace the paragraph beginning on page 6, line 13, with the following rewritten paragraph:

In a manner described earlier, a wide diversity of catalytic complexes can be converted in to solid material by a common protocol. Such solid materials are found to be stable under commonly encountered reaction environments. In another respect, soluble catalysts for diverse classes of reactions, such as for instance hydrogenation, hydroformylation, carbonylation, olefination, telomerization, isomerization, ~~isomarization~~ oxidation, etc. can be solidified. Yet another aspect of the present invention is the formulation of this material and a solid support to form a catalyst. The support involved here can be chosen independent of catalytic entity being formulated and catalytically inactive additive that is admixed. The most interesting aspect of the present invention is that said catalytic formulation alternatively termed as catalytic ensemble or catalytic assembly, remain as a solid without its components being disintegrated by dissolution. Said ensemble can be employed for catalyzing chemical reactions in slurry or fixed bed reactor configurations.

Please replace the paragraph beginning on page 7, line 27, with the following rewritten paragraph:

**Figure 3** is the schematic of the continuous ~~continues~~-liquid extractor for solids wherein, **a** is the unidirectional gas bubbler connected to condenser, **b** is the condenser, **c** is the extraction vessel holding magnetic needle and solid to be leached/extracted, **d** is the magnetic stirrer unit, **e** is the vessel holding extraction liquid, and **f** is the high temperature bath

Please replace the paragraph beginning on page 8, line 21, with the following rewritten paragraph:

In one embodiment of the ~~invention-invention~~, ~~provides~~ a novel heterogeneous catalytic composition comprising a solid support having deposited thereon a catalytically active material which is practically insoluble in variety of liquid media is provided, the said solid material consisting of catalytically active anionic entities with group IIA metal ions and the catalytic active material is molecularly well defined.

Please replace the paragraph beginning on page 9, line 9, with the following rewritten paragraph:

In yet another embodiment of the invention, there is provided ~~provides~~ a catalyst comprising ~~a~~ of solid support having deposited thereon catalytically active entity which remains as a stable composite solid in gas, liquid and gas-liquid phases and the liquid phase is selected from organic, aqueous, fluorous ~~fluors~~, non-aqueous ionic liquids and supercritical fluid phases or mixture thereof containing reactants, products and promoters.

Please replace the paragraph beginning on page 9, line 21, with the following rewritten paragraph:

In yet another embodiment, the catalytically ~~the catalytically~~ active entity is an anion having two or more negative charges and is independently selected from metal complexes, quaternary compounds, metaloxoanions, polyoxometallates and combinations thereof.

Please replace the paragraph beginning on page 15, line 24, with the following rewritten paragraph:

The reaction media as said earlier is quite broad class of liquids and may be selected depending on solubility of substrates and other components as well as it should provide clean recovery of products. The liquids usable as reaction media are exemplified but not limited by petroleum fractions of different boiling ranges, cyclo alkanes such as cyclohexane, cycloheptane, cyclodecane, aromatics such as benzene, toluene, xylenes, ethyl benzene, butylbenzene, alcohols including methanol, ethanol, propanol, butanol, amyl alcohols (linear and branched) higher alcohols, cyclohexanol, phenol, xylinol, cresol, acids such as acetic, propionic, butyric, amides such as formamide, dimethyl formamide, pyrrolidone, n methyl pyrrolidone, nitriles such as acetonitrile, propionitrile, benzonitrile, esters such as ethylacetate, methylacetate, methyl propionate, methyl benzoate methyl propionate, ethers such as diethylether, dibutyl ether, diphenylether, tetrahydrofuran, dioxane, furan, ketones such as acetone, methylethylketone, pentane 2 one, cyclohexanone, nitroaliphatics such as nitromethane, nitroethane, nitropropane, nitroaromatics such as nitrobenzene, 2-nitrotoluene, halogenated solvents such as dichloromethane, chloroform, carbon tetra chloride, 1,2 dichloroethane, chlorobenzene, dichlorobenzene ~~diehlobenzene~~ other high boiling solvents used for specific purpose include, hexadecane, octadecane, hexatracontane, squalene, chlorinated hydrocarbon oil, liquid paraffin, mineral oil, naphthalene, phenanthrene, methyl naphthalene, high boiling substituted and non substituted organic alcohols, glycol, polyglycols, ethers, polyethers, such as glycerol, carbitol, dulcitol, erythritol, polyethyleneglycol, propyleneglycol, diglycerol, diethyleneglycol, polypropylene glycol, tetraethyleneglycol, 2-ethyl-1,3-hexanediol ~~2-ethyl-1-3-hexane diol~~, 1,5 pentanediol, methoxypolyethylene glycol, diethylene glycolmonomethyl ether, polybutyleneglycol, 1,2,4-butanetriol, polyphenylether, methylbenzylether, bis(phenoxyphenyl)ether, tetraethylene glyco

dimethylether, high boiling esters such as diisooctylphthalate, dibutyl phthalate, dioctylphthalate, bis(2-ethylhexyl) phthalate, dinonyl phthalate, butyl benzyl phthalate, bis(2-tetrahydrofurfuryl) phthalate, dipropyl tetrachloro phthalate, dioctyl sebacate, bis(2-ethylhexyl)sebacate, inorganic solvents employable are water, room temperature ionic liquids, fluorous ~~fluors~~-solvents and super critical dense phases. It is also possible that combination of one or more solvent media be used for reactions depending on solubility of reactants and products. The criteria for selection of solvent are chemical physical requirements of the reaction than the catalyst formulation components. The catalyst formulation as a whole is stable in diverse reaction media so practically any liquid can be used as solvent of the reaction as in case of conventional heterogeneous catalysts. Of course it is understood that for optimum performance of the catalyst very few liquids are suitable and must be selected accordingly.

Please replace the paragraph beginning on page 37, line 25, with the following rewritten paragraph:

The final formation of composite catalyst can thus be carried out by precipitation of catalytically active material on the support surface. The formation of catalyst by precipitation or co-precipitation ~~co-precipitation~~ is thus centrally important in this respect. However precipitation is a complex phenomenon and demand several ancillary techniques to be developed in order to deposit catalyst on the support surface. Nevertheless, for several catalytically relevant materials especially for support materials precipitation is most frequently applied method. In this respect such precipitation is troublesome as it may generate clusters and particles in the bulk of liquid. Dealing specifically formation of solid catalytically active material is better described by term co precipitation as two components categorized as group IIA metal ion and poly anionic entity when interacted yields a precipitate. Co-

~~precipitation~~ ~~Co-precipitation~~ is extremely suitable technique for generation of uniform distribution of such material on the support material, as ~~stoichiometry~~ ~~stoeichiometry~~ of interacting species is definite. From earlier experiences it is known fact that co-precipitation ~~eo-precipitation~~ can provide good dispersion of the support surface which is otherwise difficult to achieve catalyst assembly that is under consideration. Thus the bulk co-precipitation ~~eo-precipitation~~ process needs to be modified to achieve assembly of composite catalyst system.

Please replace the paragraph beginning on page 47, line 9, with the following rewritten paragraph:

The group IIA metal cation is selected from compounds of  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ . The process for formation of catalyst in coating pan as described earlier wherein the solvent employed to form solutions is preferably aqueous, water miscible organic or mixture thereof. Such solutions according to the process are sprayed simultaneously ~~simultaneously~~ or sequentially.

Please replace the paragraph beginning on page 47, line 13, with the following rewritten paragraph:

Irrespective of the processes employed to form catalytic formulation said solid catalytic ensemble could be employed to catalyze diversity of reactions in gas phase or in liquid slurry. The catalyst being robust solid provides an opportunity to select suitable reactor configuration for manufacture of organic compounds in variety of reactor configurations such as fixed bed, trickle ~~trickle~~-bed, fluidized bed and slurry reactors depending on the physical state and properties of reactants and products.

Please replace the paragraph beginning on page 48, line 5, with the following rewritten paragraph:

The supported catalysts according to the invention are extremely active as is born out by the tests in the description, which is given in the examples, which follow. In fact these examples relate to the application of such supported catalysts to the diversity of reactions catalyzed by different mechanisms and according to known theories of molecular catalysts. A comparison of the reactions of these supported catalysts in homogeneous phase establishes that while retaining catalyst activity to considerable extent facile separation can be easily achieved. This makes catalyst suitable for continuous process thereby enhancing catalyst process economics. The said catalyst formulation being inherently solid can be easily recovered after the desired catalytic conversion in the heterogeneous phase. They can then be reused to catalyze new charge of reactants, this operation being either continuous ~~continues~~ or repeatable wherein the catalyst can be recycled for several times. The advantageous fact is catalytic formulation being repeatable several times without their activity being appreciably degenerating.

Please replace the paragraph beginning on page 51, line 11, with the following rewritten paragraph:

The technique of solid catalyst formulation is established in the present invention according to which the solid catalyst can be formulated and applied for catalyzing reactions in a diversity of solvents. The catalytic formulation referred herein was applied to a variety of reactions according to yet another embodiment. An exemplary reaction class for which catalytic formulation was employable is described in subsequent sections. Reaction classes that are described here are only exemplary and limited by scope of catalytically active entity as said earlier. Variety of reaction classes described herein are intended to outline the scope of



catalytic formulation that is under consideration wherein emphasis given on catalyst separation, stability and convenience of operation when applied to manufacture of plurality of organic compounds. Classes of reaction described herein are hydroformylation, hydrogenation, carbonylation, carbon-carbon bond formation by Heck and Suzuki type reactions, isomerization~~isemarization~~, epoxidation, Wacker oxidation, Michel addition and Knovengel condensation.

Please replace the paragraph beginning on page 52, line 18, with the following rewritten paragraph:

Double bond isomerization~~isemarization~~ is useful reaction in converting olefins to isomerized~~isemarized~~ olefins. Various transition metal complexes catalyze this type of reaction. Metal complexes useful in this respect are platinum, palladium, rhodium and cobalt. The catalytic formulation of present invention is also useful in catalyzing this reaction.

Please replace the paragraph beginning on page 54, line 10, with the following rewritten paragraph:

As catalyst lifetimes are better understood through working with a particular catalyst formulation in repeated recycling in either laboratory or in commercial settings it may be further desirable to regenerate catalyst time to time either by washing with suitable liquid or by specific chemical treatment. Continuous~~Continues~~ reaction processes are also practicable for applicants preferred catalysts in view of their insolubility and resistance to leaching or other disintegration. Such processes can be designed and implemented using common and known procedures in the art.

Please replace the paragraph beginning on page 59, line 5, with the following rewritten paragraph:

Sulfonation of tribenzyl phosphine was carried out analogous ~~analegous~~ to triphenyl phosphine except exact degree of sulfonation was not established reaction mixture containing di and tri sulfonated phosphine was used for further experiment.

Please replace the paragraph beginning on page 59, line 10, with the following rewritten paragraph:

4.95 g. (12 mmol) of diphenylphosphino propane was dissolved in a solution of 4 g. (64.7 mmol) orthoboric acid in 37.5 ml (98%) reaction mixture was cooled to 0 °C, to this 65% oleum 67.5 ml was added drop wise over a period of 2 hours. After addition reaction mixture was brought to 25 °C and stirred for 48 hours. After this reaction mixture was brought to 0 °C and hydrolyzed with 50 ml degassed water. This solution was neutralized with 50 % w/w sodium hydroxide in water until pH 7 and formed precipitate was removed by filtration and mother liquor was concentrated to 30 ml and diluted with 100 ml methanol and refluxed for 2 hours. Resulting precipitate was removed by filtration. The extract in methanol was evaporated to obtain a solid which was suspended in 100 ml methanol and to this 5 g microcrystalline cellulose avicel was added followed by 1 ml conc H<sub>2</sub>SO<sub>4</sub> and refluxed for 6 hours under argon blanket ~~blaneket~~. Solution was cooled and filtered ~~filtured~~ to remove avicel. To this 5 g. avicel was again added and refluxed for another 6 hours suspension was filtered and methanolic extract was neutralized with 50 % NaOH w/w and filtered. Solution was evaporated to obtain a white compound.

Please replace the paragraph beginning on page 60, line 4, with the following rewritten paragraph:

Equip a three litre three-necked flask with a sealed mechanical stirrer, a reflux condenser and a thermometer. Flask was cooled to 0 °C in ice salt bath. Reaction vessel was charged with 24.2g (0.1 mol) diphenic acid and 15.12 g (0.4 mol) sodium borohydride to this solid powder 200 ml dry tetrahydro furan was added in such a way that there is minimum effervescence. After 1 hour suspension becomes uniform and to this (0.2 mol H<sub>2</sub>SO<sub>4</sub> in 100 ml tetrahydrofuran was added over a period of 2 hours while maintaining temperature at 0 °C. after addition was over mixture was allowed to stir ~~stir~~ for 24 hours at room temperature. To this white suspension 100 ml 30 % NaOH was added and refluxed for 4 hours and liquid was brought ~~brought~~ to room temperature and extracted with chloroform to yield white solid ~~solide~~. Which was used further without purification.

Please replace the paragraph beginning on page 60, line 14, with the following rewritten paragraph:

Diol intermediate (0.08 mol) from above said preparation was dissolved in chloroform and transferred to two necked flask attached with condenser and guard tube, pressure equalizing addition vessel. One drop of pyridine was added to flask and (0.2 mol) thionyl chloride was dissolved in 25 ml chloroform and charged in addition vessel. Thionyl chloride was added to round bottom flask at room temperature. During addition considerable amount of sulfur dioxide and hydrogen chloride escaped from guard tube. The temperature of the flask was raised until chloroform started refluxing. After 5 hours reaction was quenched by addition of water. Chloroform was extracted ~~extracted~~ with bicarbonate solution followed by water and dried by passing through bed of sodium sulfate. Chloroform was evaporated under

vaccume at 50 °C to ~~yield yild~~-yellow colored oil (irritant and inflammatory to skin), which was distilled, in high vaccume to yield pale yellow colored oil.

Please replace the paragraph beginning on page 63, line 19, with the following rewritten paragraph:

To a reaction system ~~comprising comparing~~ a solution of dimethyl maleate (50 g.) in chloroform (100 ml) was added a solution of bromine (15 ml) in chloroform 100 ml over a period of 2 hours. The reaction mixture was stirred for 2 hours at the end of reaction mixture was washed twice with 100 ml saturated sodium thiosulphate and then twice with 100 ml water. Organic part was passed through 5 g. sodium sulphate and ~~subsequently sub-sequently~~ treated with activated charcoal. Chloroform was stripped off to yield 60 g oil.

Please replace the paragraph beginning on page 63, line 25, with the following rewritten paragraph:

Subsequent reaction was set up with 250 ml. three necked glass vessel equipped with addition funnel magnetic stirrer and rubber septum. Assembly was flushed with argon. To this vessel finely cut lithium ribbon (500 mg.) was added and assembly was ~~evacuated evaeuuated~~ and ~~refilled refilled~~ with argon. To this ~~assembly, asseby~~ 50 ml tetra hydrofuran was added with gas tight syringe maintaining argon blanket 8.3 ml chlorodiphenyl phosphine was placed in addition funnel set up was evacuated and refilled with argon contents of addition funnel were dropped in the lithium suspension, during lithium dissolution solution started assuming red color and ~~reaction reaection~~ mixture was stirred for 4 hours after complete dissolution of lithium.